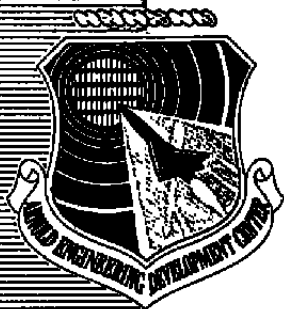


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High Resolution Spectroscopy of $C^{13}O^{16}$ in Gas Mixtures

H. C. Walker, Jr.
Sverdrup Technology, Inc.

March 1985

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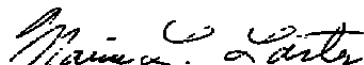
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PREFACE

The work reported herein was conducted by the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), Arnold Air Force Station, TN 37389. The results were obtained by Sverdrup Technology, Inc., AEDC Group, operating contractor for the propulsion test facilities at AEDC under Sverdrup Project No. E32M-C32. The Air Force Program Manager was Capt. F. Tanji. The Sverdrup Project Manager was H. C. Walker, Jr. The manuscript was submitted for publication on January 17, 1985.

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1.0 INTRODUCTION

A nonintrusive method of measuring the concentration and temperature of specific molecules in the exhaust stream of rocket and turbine engines is being sought to replace the probe methods currently in use. These current methods provide results which are subject to question because the probe itself may chemically alter the exhaust gas composition. The tunable diode laser (TDL) spectrometer system is being developed as a possible replacement for the probes.

TDL measurements can be made by passing the laser beam through the exhaust gases as they exit the engine. The energy absorbed from the laser beam is related to species concentration; that is, the absorption is proportional to the number of absorbing molecules in the beam. The absorption also depends on wave number (line shape), as well as a line strength function, which is temperature dependent. The line shape is affected by collisions with the absorbing molecules; therefore, the absorption is a function of the partial pressure of each gas present. Each gas present has a characteristic effect on the shape of the absorption line.

To make accurate measurements, the instrument should be capable of recording true line shapes. The TDL, which has a line width of the order of 10^{-4} wave number, provides, for all practical purposes, the true line shape (many absorption lines have a full width at half maximum (FWHM) of 0.1 to 0.2 wave numbers). Additionally, with the TDL the exhaust gas temperature can be determined by the two-line technique utilizing the temperature dependence of the line strength function.

In the past the TDL spectroscopy system has been used in the laboratory to make a detailed study of representative lines of the CO fundamental band at $4.7\ \mu\text{m}$. These lines can be used to measure low concentrations of CO (a few hundred parts per million) as it exists in the exhaust of turbine engines. This method has been calibrated for CO broadened by nitrogen, carbon dioxide, and water vapor (Ref. 1).

In the exhaust plume of tactical missiles the concentration of CO is expected to be much higher (several percent) than in turbine engine exhausts ($> 500\ \text{ppm}$). The lines previously examined would be saturated (absorption greater than 95 percent) at the higher concentrations. Tactical missile rocket exhausts will require measurements to be made on absorption lines which do not absorb radiation as strongly as in the fundamental band of the principal isotope, $\text{C}^{12}\text{O}^{16}$. In the present report, measurements on the $\text{C}^{13}\text{O}^{16}$ isotope of CO at $4.7\ \mu\text{m}$ will be described. The natural abundance of $\text{C}^{13}\text{O}^{16}$ in CO is approximately 1 percent and the spectral absorption lines are offset from the $\text{C}^{12}\text{O}^{16}$ lines (greater than $0.4\ \text{cm}^{-1}$) such that overlap of lines does not have to be considered. This makes $\text{C}^{13}\text{O}^{16}$ a natural choice for measuring high concentrations of CO (several percent).

Measurements of pressure broadening parameters were made on the P(17) and P(16) lines of the (1-0) band of $C^{13}O^{16}$ using 20-percent CO in nitrogen at temperatures ranging from 300 to 900 K. The $C^{12}O^{16}$ broadening of $C^{13}O^{16}$ was assumed to be the same as $C^{12}O^{16}$ self broadening in the data analysis, and the nitrogen broadening of $C^{13}O^{16}$ was measured as a function of temperature. The results, which were taken at various pressures and temperatures, were extrapolated to standard temperature and pressure. A discussion of the pertinent theory, experimental techniques, and results follows.

2.0 THEORY

The experimental data can be analyzed within the framework of well-established theory. For transmission of radiation through a sample gas, the transmitted radiation at a frequency w is related to the incident radiation by the Lambert-Beer law:

$$I(w) = I^0(w) \exp(-k(w)l) \quad (1)$$

where

$I(w)$ = spectral intensity transmitted by sample

$I^0(w)$ = incident spectral intensity

$k(w)$ = absorption coefficient

l = optical path length, cm

w = frequency of radiation in wave numbers, cm^{-1}

At very high resolution such as with the TDL spectrometer, the true line shape can be obtained from a transmission measurement. The line strength or line intensity, S , is defined for an isolated absorption line by the equation:

$$S = \int_{-\infty}^{\infty} k(w)dw \quad (2)$$

The line strength can be calculated for a given transition by the approximate Herman-Wellis formula which is used in the form (Refs. 2 and 3):

$$S^{v''J(T)} = S^0 \left(\frac{273.15}{T} \right) \left(\frac{W}{W^0} \right) \exp \left(\frac{-E^{v''(J)}}{kT} \right) \left(1 - \exp \left(\frac{-hcw}{kT} \right) \right) A \left(\frac{v'' + 1}{Q(T)} \right) \quad (3)$$

S^0 = band strength at 273.15 K and 1.0 atm, $\text{cm}^{-1}\text{atm}^{-1}$

w = frequency of given transition, cm^{-1}

w^0 = frequency of the band center, cm^{-1}

$E^{v''}(J)$ = transition ground state energy, cm^{-1}

$Q(T)$ = total internal temperature dependent partition function

T = temperature, $^{\circ}\text{K}$

A = rotational index

v'' = vibrational quantum number for lower state

h = Planck's constant

c = speed of light

k = Boltzmann's constant

To determine the absorption coefficient, it is necessary to determine the line shape function as well as the line strength. The parameter to be determined which specifies the line shape function is the half-width. This parameter is defined as one-half of the width of the absorption coefficient curve at half-height. There are two limiting cases to be considered corresponding to low pressure and high pressure. The doppler function gives the line shape in the low pressure limiting case of no collisional broadening.

$$k(w) = \left(\frac{fn_2}{\pi}\right)^{1/2} \left(\frac{S}{\gamma_D}\right) \exp \left[- (w - w^0)^2 \frac{fn_2}{\gamma_D^2} \right] \quad (4)$$

The doppler width is given by:

$$\gamma_D = \left(\frac{2kTfn_2}{Mc^2}\right)^{1/2} w^0 \quad (5)$$

where M is the mass of the absorbing molecule. The Lorentzian function gives the line shape in the high-pressure limiting case where collision broadening is dominant:

$$k(w) = \left(\frac{\left(\frac{S}{\pi}\right) \gamma_L}{(w - w^0)^2 + \gamma_L^2} \right) \quad (6)$$

γ_L is the Lorentz half-width. Most measurements will fall between the two limiting pressures and can be covered by a general equation known as the Voigt line shape:

$$k(w) = S \left(\frac{\left(\frac{\ln 2}{\pi}\right)^{1/2}}{\gamma_D} \right) \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-y^2)}{(a^2 + (x - y)^2)^2} dy \quad (7)$$

where a is the Voigt parameter:

$$a = (\ln 2)^{1/2} \frac{\gamma_L}{\gamma_D}$$

and

$$x = \frac{(w - w^0)(\ln 2)^{1/2}}{\gamma_D}$$

is the normalized distance from line center frequency. These equations can be found in texts such as Ref. 4.

The pressure broadening is attributable to self broadening and foreign gas broadening. The self broadening is due to collision with like molecules while foreign gas broadening is produced by collisions with other species present in the mixture. Every gas used to broaden the absorption coefficient curve can be characterized by the parameter γ_L ($\text{cm}^{-1}\text{atm}^{-1}$), which is the collisional or Lorentz half-width attributable to broadening of the absorbing molecule by the foreign gas at 1 atm pressure. For the case of several foreign gases present, the Lorentz half-width is calculated by (Ref. 4):

$$\gamma_L = \sum_i \gamma_{Li} P_i \quad (8)$$

The P_i and γ_{Li} are the partial pressure and Lorentz half-width for the i^{th} foreign gas present in the mixture.

A computer program was developed at AEDC which calculates the Voigt line shape which best fits the absorption data obtained in the test situation. The line strength and the half-width parameters are calculated from the Voigt fit parameters and are printed out by the program.

To compare line strengths for the same line but at different temperatures, an equation relating $S(T)$ to $S(T_0)$, where T_0 is some reference temperature, is used (Ref. 5):

$$S(T) = S(T_0) \left(\frac{T_0}{T} \right) \exp \left(- \left(\frac{E''(J)}{k} \right) \left(\left(\frac{1}{T} \right) - \left(\frac{1}{T_0} \right) \right) \right) \left(\frac{Q(T_0)}{Q(T)} \right) \left(\frac{1 - \exp\left(-\frac{hcw}{kT}\right)}{1 - \exp\left(-\frac{hcw}{T_0k}\right)} \right) \quad (9)$$

The concentration of the absorbing molecule can be obtained from $S^0P = S$, where S is the absorption line strength obtained from the Voigt profile in cm^{-2} ; S^0 is the calculated absorption line strength from Eq. (3) in $\text{cm}^{-2}\text{atm}^{-1}$; and P is the partial pressure of the absorbing molecule in the beam path in atmospheres.

Data taken at different temperatures can be used to compute the half-width at a standard temperature by fitting the γ_L to

$$\gamma_L(T) = \gamma_L^0(T_0) \left(\frac{T}{T_0} \right)^{-N} \quad (10)$$

a relationship determined by Birnbaum (Ref. 6) that has been used successfully by others for the temperature dependence of CO half-widths.

In addition to making concentration measurements, it is also possible to make nonintrusive temperature measurements of combustion gases with the TDL spectrometer. The two-line technique uses two vibration-rotation lines which originate from different vibrational levels and are close enough in frequency that their absorption can be measured in one scan of the TDL. By comparing the ratio of the experimental line strengths to the ratio of the line strengths obtained from Eq. (3), the temperature of the combustion gases can be determined.

3.0 EXPERIMENT

The absorption line shape data were taken with a Laser Analytics LS-3 high resolution tunable diode laser absorption spectrometer. A schematic of the LS-3 system is shown in Fig. 1. The diode lasers, which are manufactured from single crystals grown from lead salt compounds, are contained in a temperature-controlled cold head which can be operated

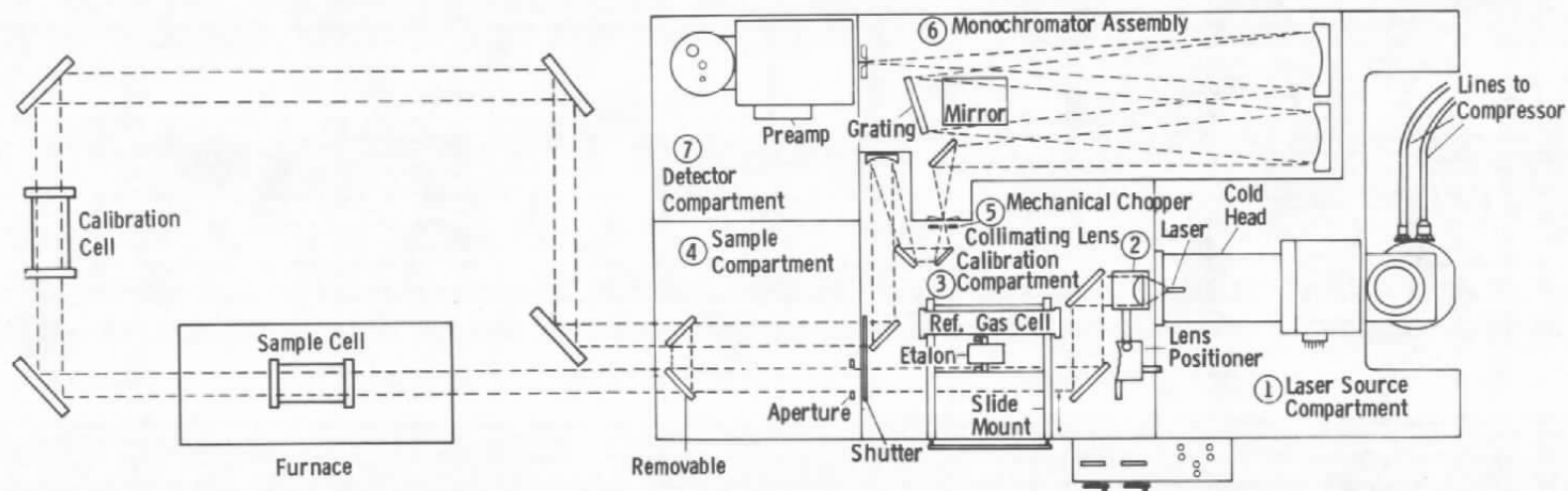


Figure 1. Laboratory optical system.

from 10 to 100°K. The diode lasers are obtained from Laser Analytics and have user-specified tuning ranges of 10, 20, and 50 cm^{-1} . The diode lasers are tuned through this range by changing the temperature of the diode laser and the diode injection current. A 1°K change in temperature will cause a 4 cm^{-1} change in laser output. When the diode laser output is tuned to the wave number of an absorption line by adjusting the cold head temperature, the laser output can be tuned across the line with joule heating produced by modulating the diode injection current. The laser output contains several modes with a minimum multimode power of 0.1 mw. The line width of each mode is approximately $3 \times 10^{-4} \text{ cm}^{-1}$. The individual modes are typically 1 cm^{-1} apart, allowing a specific mode to be selected with a 0.5-m grating monochromator having 0.5 cm^{-1} resolution. Each mode can be tuned over a range of approximately 1 cm^{-1} .

The laser output is formed into a collimated beam by the f/1 collimating lens. A 3-in. germanium etalon, slide mounted, can be introduced into the collimated beam. The etalon produces fringes with a spacing of 0.0163 cm^{-1} which are used to provide a precise wave number calibration of the laser beam.

The collimated beam is directed out of the TDL system to a copper absorption cell mounted in a furnace. The optical cell has sapphire windows and the vacuum seal is obtained by crushing a platinum o-ring between the cell and window (Fig. 2). The temperature of the gas in the absorption cell is monitored by a thermocouple inside the cell. The beam is subsequently directed through a calibration cell and back into the TDL system. Inside the TDL system is a 400-Hz tuning fork chopper and a 0.5-m grating monochromator. In addition to separating the laser modes, the monochromator provides a coarse (0.5 cm^{-1}) absolute wave number calibration. The tuning fork chopper, used in conjunction with a lock-in amplifier, increased the signal-to-noise ratio of the detector signal.

The output mirror of the monochromator focuses the beam on the entrance slits of the detector. The detector used in this work was a liquid nitrogen-cooled indium antimonide (InSb) infrared detector. The peak responsivity for this detector is at 2080 cm^{-1} . The detector unit includes adjustable optics for focusing the beam onto the 2 mm^2 active area of the detector as well as an impedance match amplifier.

In the present work, measurements of the half-width of the P(17) and P(16) absorption lines of the (1-0) vibrational band of $\text{C}^{13}\text{O}^{16}$ at 2029.2 and 2033.4 cm^{-1} (Ref. 7) were accomplished as a function of temperature and foreign gas pressure. The pressures used were 1/3, 2/3, and 1 atm, and the temperature range for the measurements was 300 to 900 K. The CO and N2 mixture was obtained commercially; the concentration of CO was 19.988 percent, and the balance was N2.

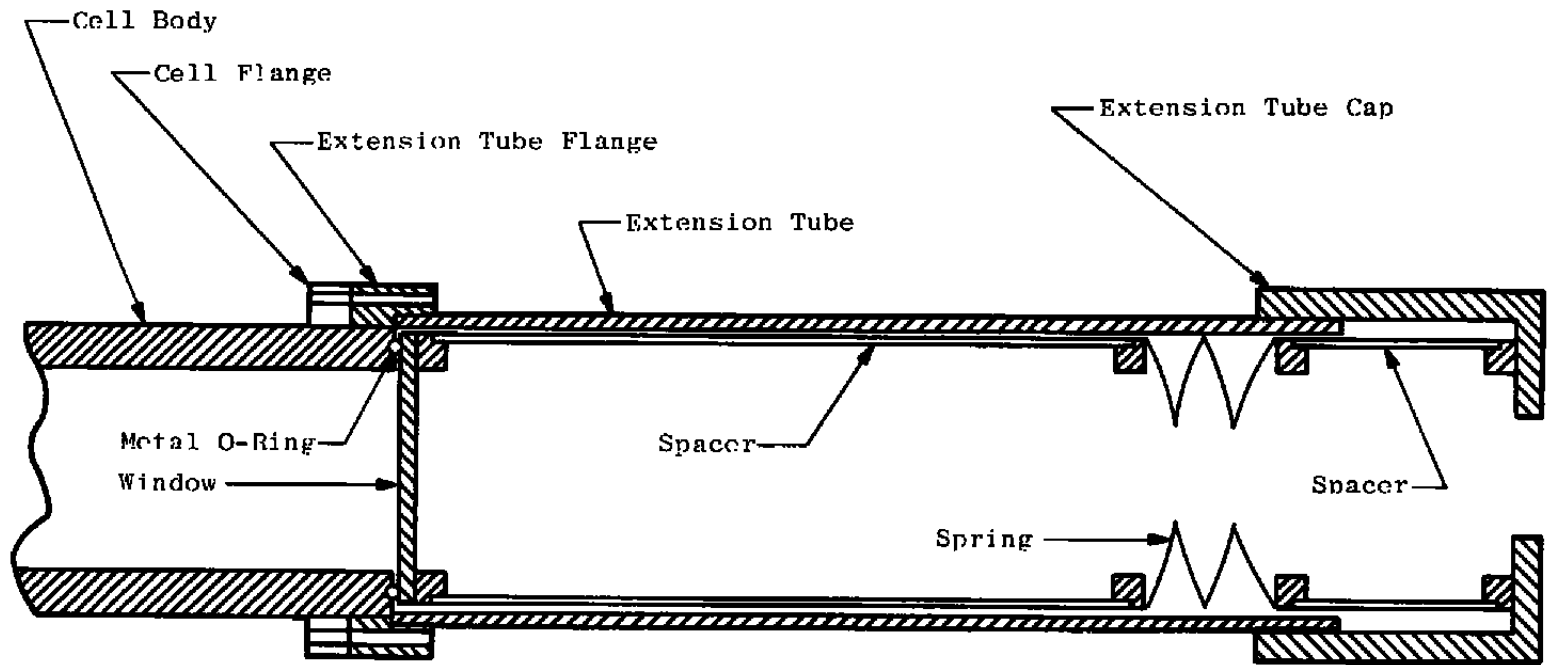


Figure 2. Hot cell.

For each spectrum recorded, the CO/N₂ mixture was admitted into the evacuated sample cell after the laser had been tuned to the center of the absorption line. Following each data point, the cell was pumped out and a 100-percent transmission scan was recorded. Figure 3 shows an example of raw data, including the 100-percent transmission and etalon traces.

The data were digitized and recorded on magnetic tape in the laboratory by a 12-bit resolution Hewlett Packard 2100 computer. Analysis was accomplished later on the AEDC central computer.

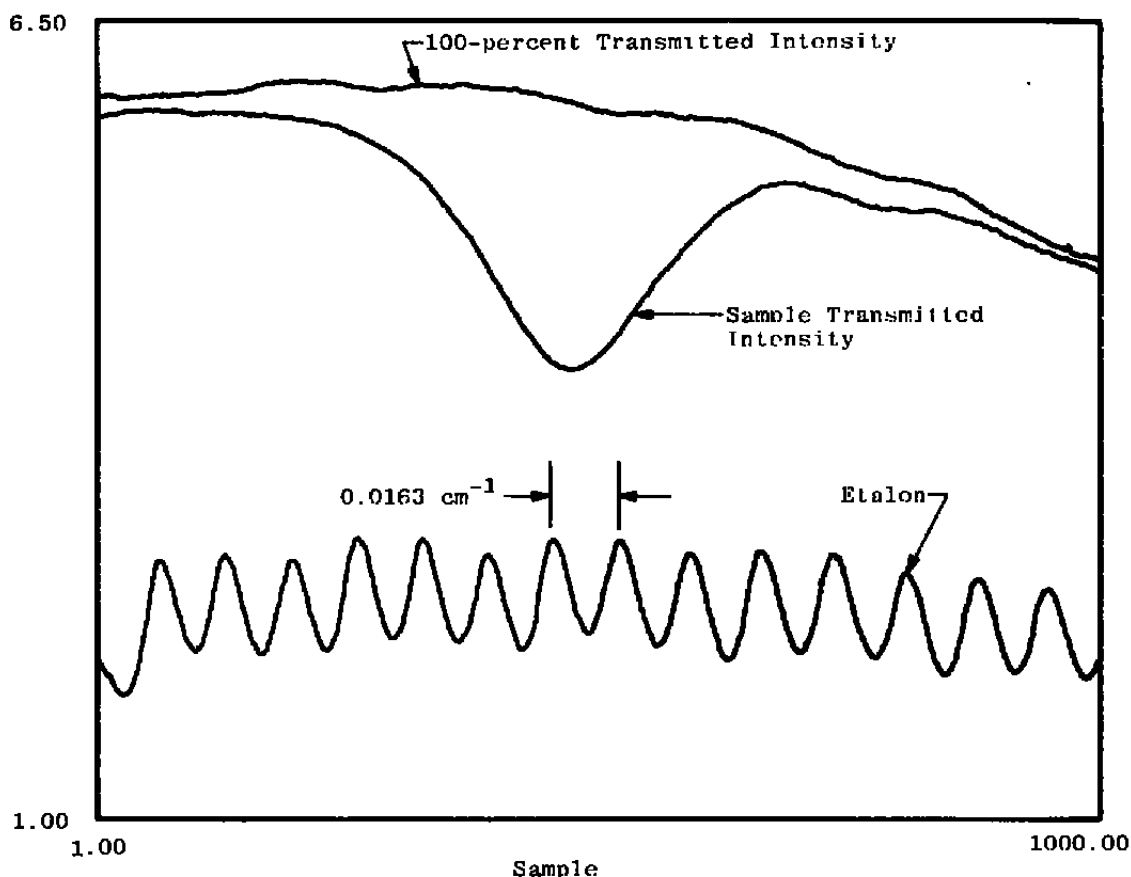


Figure 3. Typical data point showing the various transmission measurements needed to evaluate each data point.

4.0 RESULTS AND DISCUSSION

The broadening parameters at the various gas temperatures were obtained by performing a nonlinear least-square fit of the spectral intensity profiles taken with the tunable diode laser spectrometer to the function given in Eq. (1) using the Voigt profile for the absorption

coefficient. The two fit parameters obtained are "S" and "a". The collision-broadening parameter γ_L^0 is obtained from "a". $\gamma_{N_2}(T)$ (the foreign gas-broadening parameter) is obtained by using Eq. (8) and the following quantities: $\gamma_L(T)$, measured pressure, measured temperature, and an assumed CO self-broadening parameter. The temperature-dependent foreign gas-broadening parameters are then least-square fitted to Eq. (10) to obtain the foreign gas-broadening parameters at standard temperature and the temperature exponent N_i .

The self-broadening parameters which account for broadening attributable to collision between CO molecules at the various temperatures used in the data analysis were obtained from the use of Eq. (10) and the self-broadening data from Ref. 8.

Figure 3 shows a typical data point which consists of a measurement with the cell evacuated, a measurement with the gas present, and the etalon measurement. The transmission with the sample cell evacuated gives the amount of radiation transmitted from the diode laser through the optical system to the detector without the gas sample present in the beam path. The transmission with the gas present shows the amount of radiation which is transmitted through the system when the optical cell is filled with absorbing gas. The difference between the two curves gives the amount of radiation absorbed by the gas sample. The transmission with the etalon is taken with the optical cell evacuated and the germanium etalon in the beam. Adjacent peaks on the etalon transmission curve at 0.0163 cm^{-1} apart; this allows the diode injection current to be related to the frequency in wave numbers.

Figure 4 shows the same data point after analysis. The transmission with the cell evacuated has been smoothed, and the Voigt profile which best fits the sample transmission curve has been calculated. As can be seen, the fit between the Voigt profile and the sample transmission was very good for this point. The foreign gas-broadening parameters were obtained from the data by adjusting the integrated absorptance "S" and the ratio of the line widths "a" to make the Voigt profile, Eq. (7), fit the sample transmission. The data point shown is for approximately 2/3 atm total pressure of CO/N₂ at 603 K.

Data were taken on the P(17) and P(16) absorption lines of the fundamental band of $\text{C}^{13}\text{O}^{16}$ at temperature intervals of 100 K from 300 to 900 K. Fifteen data points were taken at each temperature with 20-percent CO in a total pressure of approximately 1/3, 2/3, and 1 atm. Since the theory predicts that the half-width will vary linearly with pressure [Eq. (8)], each half-width determined by the fit to the Voigt profile could be adjusted to give the half-width at atmospheric pressure. All the data were taken at temperatures within a few degrees of a multiple of 100 K. The half-widths determined from the Voigt profile were then fitted to

Eq. (10) to determine the value of N . Equation (10) and the determined value of N were then used to adjust the data a few degrees to an even multiple of 100 K.

Since the gas mixture contained approximately 20-percent CO, the CO self-broadening had to be accounted for. It was assumed that $C^{12}O^{16}$ broadening of $C^{13}O^{16}$ was the same as $C^{12}O^{16}$ self-broadening. The nitrogen broadening parameter was calculated using the experimental values measured here and subtracting the $C^{12}O^{16}$ broadening parameter using Eq. (8).

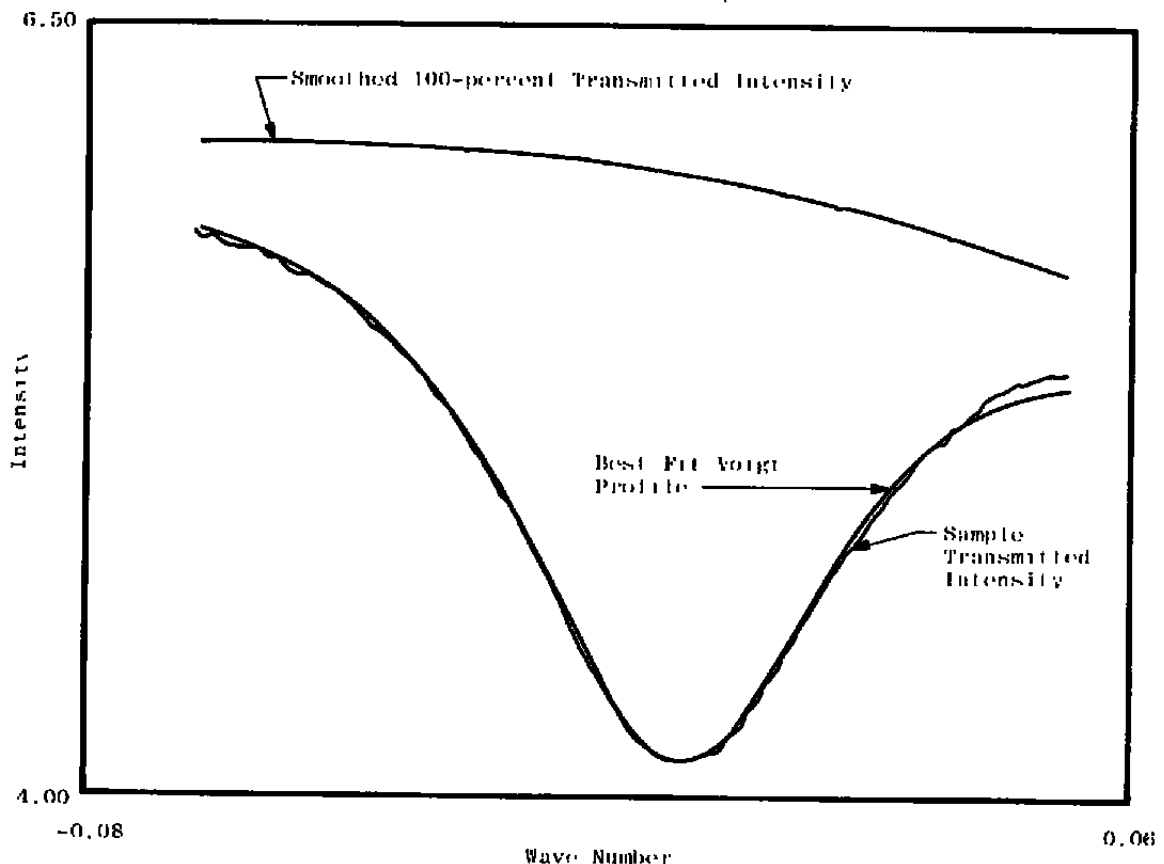


Figure 4. Data point after analysis.

The nitrogen-broadened half-width of CO is plotted versus the total pressure in Fig. 5 for representative temperatures. Theory predicts a linear relationship between γ_L and pressure, which is approximately observed in Fig. 5.

Table 1 shows the average value of the collisional foreign gas-broadening half width $\gamma_{N_2}^0$ for each temperature measured. This value has been corrected for both Doppler broadening and CO self-broadening. The probable error defined as $0.6745 (\sigma/\sqrt{N})$ where N is the

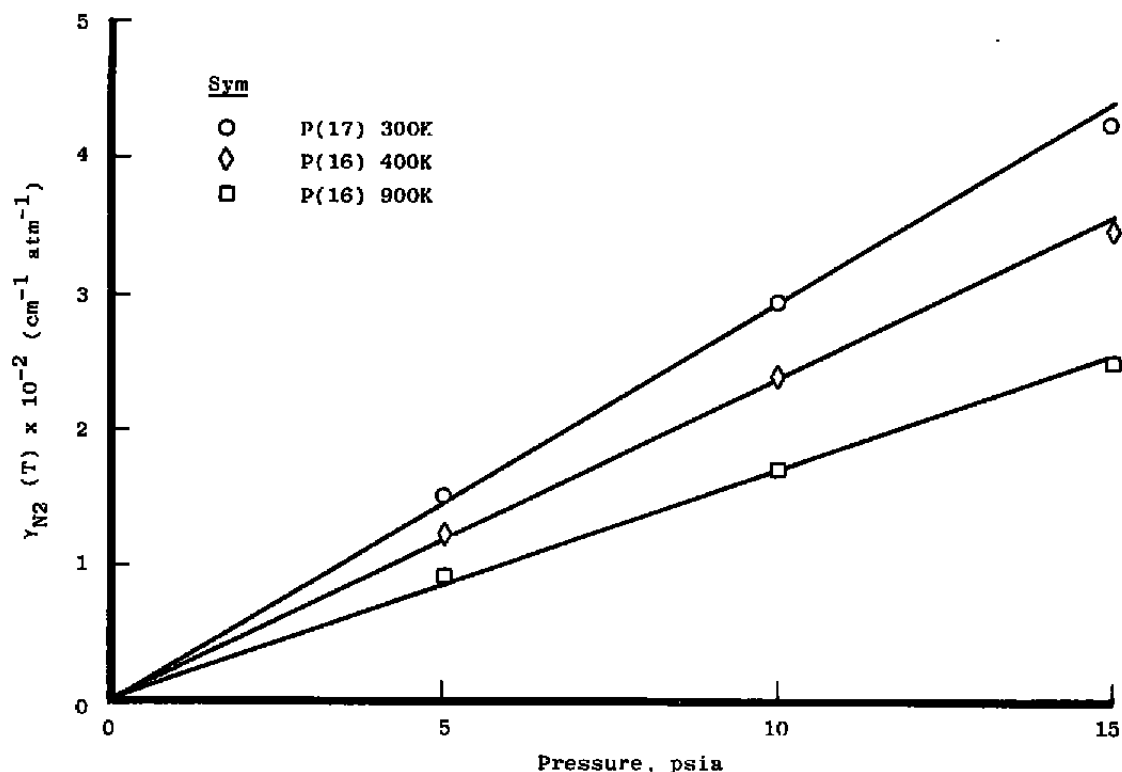


Figure 5. Collision-broadening parameter versus pressure.

number of data points shown with each value of $\gamma_{N_2}^0$ where there was enough data for the calculation. As indicated by Eq. (10), the value of $\gamma_{N_2}^0$ from Table 1 should yield a straight line when it is plotted against temperature on a log-log scale. Figure 6 is a plot of the nitrogen-broadening data for the P(17) absorption line.

Table 1. Average Half-Widths for Nitrogen Broadening of $C^{13}O^{16}$ at Temperatures Studied

Temperature (K)	P(17) $\gamma_{N_2}^0(T) \text{ (cm}^{-1}\text{atm}^{-1}\text{)}$	P(16) $\gamma_{N_2}^0(T) \text{ (cm}^{-1}\text{atm}^{-1}\text{)}$
300	0.04272 ± 0.00042	0.04113 ± 0.00027
400	0.03503 ± 0.00031	0.03570 ± 0.00032
500	0.03158	
600	0.03056 ± 0.00104	0.02865 ± 0.00023
700	0.02720 ± 0.00045	
800	0.02656 ± 0.00061	0.02585 ± 0.00028
900	0.02184	0.02497 ± 0.00033

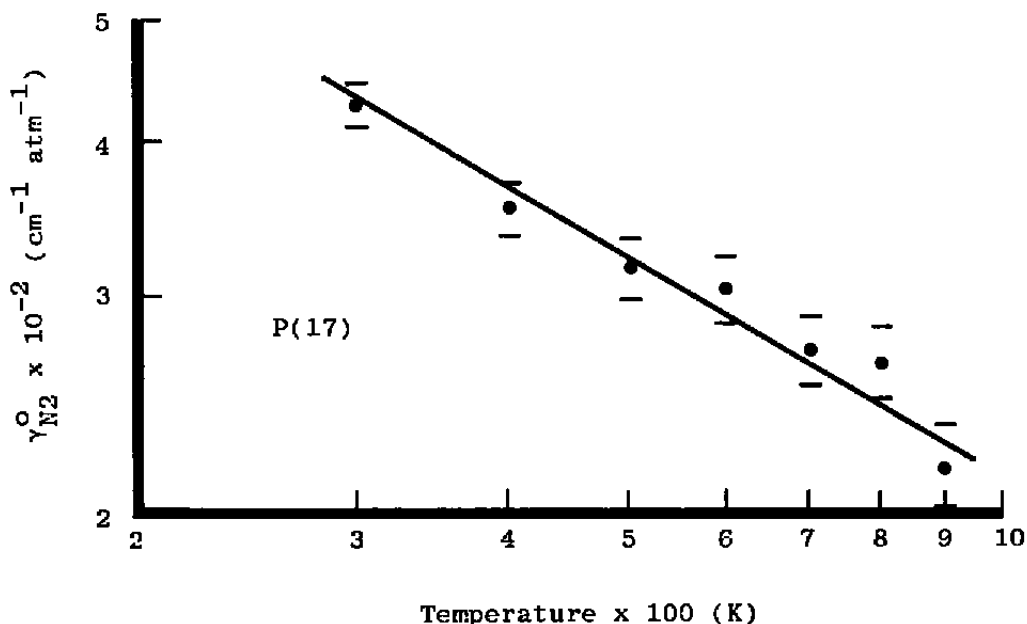


Figure 6. Collision-broadening parameter versus temperature.

Figure 7 is a plot of the same data for the P(16) absorption line. The data for the P(16) line fits a straight line much better than the data for the P(17) line.

Table 2 shows the standard conditions used for the analysis of both absorption lines. The collision-broadening half-width $\gamma_{N_2}^O(T_0)$ is the average value for standard temperature and

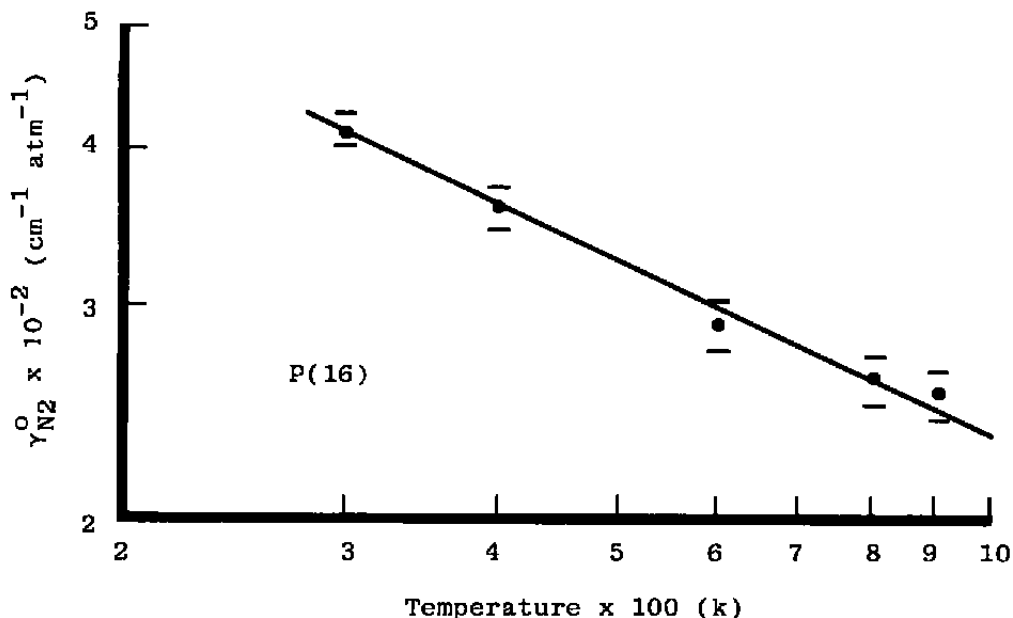


Figure 7. Collision-broadening parameter versus temperature.

pressure conditions which is calculated from all the experimental values measured in this program. The nitrogen broadening of $C^{13}O^{16}$ resulted in a $\gamma_{N_2}(T_0)$ of $0.04361 \pm 0.00022 \text{ cm}^{-1} \text{ atm}^{-1}$ for the P(17) absorption line and a $\gamma_{N_2}(T_0)$ of $0.04245 \pm 0.00014 \text{ cm}^{-1} \text{ atm}^{-1}$ for the P(16) line. There are no published values for γ_{N_2} for $C^{13}O^{16}$ with which to compare these values; however, in comparing them to values for $C^{12}O^{16}$, the values are approximately 20-percent smaller than published values.

The temperature-dependent exponents N_{N_2} obtained from fitting all experimental data for each absorption line to Eq. (10) are -0.50481 ± 0.12464 for the P(17) line and -0.45471 ± 0.01682 for the P(16) line. The standard deviation for $\gamma_{N_2}(T_0)$ is also given in Table 2, as is the average percent CO calculated from the experimental data.

Table 2. Summary of Results for Nitrogen Broadening of $C^{13}O^{16}$

	P(17)	P(16)
$T^\circ \text{ (K)}$	273.16	273.16
$N_2(T^\circ) \text{ (cm}^{-1}\text{atm}^{-1}\text{)}$	0.4361 ± 0.00022	0.04245 ± 0.00014
N	-0.50481 ± 0.12464	-0.45471 ± 0.01682
Standard Deviation	0.00177	0.00118
Percent CO	19.87	19.11

5.0 SUMMARY

In conclusion, measurements have been made of the collision broadening parameters for $C^{13}O^{16}$ broadening by nitrogen in the temperature range from 300 to 900 K. The P(17) line foreign gas-broadening parameter for nitrogen at standard temperature and pressure was determined to be $0.04361 \pm 0.00022 \text{ cm}^{-1} \text{ atm}^{-1}$ and the temperature-dependent exponent was found to be -0.50481 ± 0.12464 . The P(16) line foreign gas-broadening parameter for nitrogen at standard temperature and pressure was determined to be $0.04245 \pm 0.00014 \text{ cm}^{-1} \text{ atm}^{-1}$ and the temperature-dependent exponent was found to be -0.45471 ± 0.01682 .

To improve the measurements of high concentrations of CO using absorption by $C^{13}O^{16}$, the foreign gas-broadening parameters for $C^{12}O^{16}$ broadening of $C^{13}O^{16}$ need to be measured as a function of temperature.

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